SPACE GROUPS OF CRYSTALS OF ORTHO, META AND PARAXYLENE AT -180°C*

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Plate IV

ABSTRACT The Debye-Scherrer patterns of *o*-xylene, *m*-xylene and *p*-xylene frozen and cooled to −180°C have been photographed and analysed The analysis has given the unit cell dimensions which explain all the reflections. The densities of the substances have been determined and have been found to be 1.032, 1 030 and 1.006 gm cm^{-3} respectively for the ortho-, meta- and para compound. From these data the space group has been found in each case The crystals of *o*-xylene belong to the orthorhombic system with a 8.77, b 10.20 and c — 14.55 Å. The number of molecules per unit cell is 8 and the space group is $Pmmm$ The crystals of *m*-xylene also belong to the orthorhombic system The dimensions of the unit cell are a - 7.77, b − 8.45, c - 10.47 Å The number of molecules per unit cell is 4 The space group is $P2_12_12$ The crystals of *p*-xylene belong to the monoclinic system with a -- 7 56, b — 8.45, c -- 11.11 Å, β - 98° 57′. The number of molecules per unit cell is 4. The space group is $P2_1/m$

INTRODUCTION

In continuation of the previous work on the analysis of the Debye-Scherrer patterns of crystals of toluene (Biswas and Sirkar, 1957), pyridine (Biswas, 1958), chlorobenzene and bromobenzene (Biswas, 1958) and 1, 3, 5-trichlorobenzene (Biswas, 1959) the present investigation was undertaken to study the Debye-Scherrer patterns of *o*-xylene, *m*-xylene and *p*-xylene in the frozen state at −180°C to find out the dimensions of the unit cell, number of molecules per unit cell and the space group. Such data throw much light on the influence of intermolecular field on the individual molecules and are helpful in understanding the changes which take place in the electronic spectra of these molecules with the change from the liquid to the solid state.

EXPERIMENTAL

The chemicals *o*-xylene, *m*-xylene and *p*-xylene used in the investigation were of chemically pure quality supplied by Fisher and Co.. Debye-Scherrer patterns of the substances were taken with a low-temperature camera of special design discussed earlier (Biswas, 1958), The radius of the camera was derived from the Debye-Scherrer pattern of Al powder, and it was found to be

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4.50 cm. The specimen in the form of liquid was introduced in a Lindemann glass capillary tube of bore 0.3mm and frozen with liquid oxygen. A Seifert X-ray tube running at 32 Kv and 26 mA was used to photograph the patterns. An exposure of three and a half hours was sufficient to record the pattern with appropriate density, using Cu K_α radiation. The densities of the frozen substances at −180°C were measured by the method described earlier (Biswas and Sirkar, 1957). For the ortho variety the density was found to be 1.030 gm cm^{-3}, for the para compound 1.006 gm cm^{-3}, and for the meta compound 1.030 gm $cm.^{-3}$.

RESULTS AND DISCUSSION

(a) *Meta-xylene at* −180°C :

The Debye-Scherrer pattern is reproduced in Fig. 1, Plate IV. In the determination of unit cell dimensions of ortho, meta and para xylene from the Debye-Scherrer patterns, Lipson's method (Lipson, 1949) was first tried and when this method showed the lattice to be other than orthorhombic, Ito's method (Ito, 1950) was applied. The patterns could not be assigned to any lattice having a symmetry higher than that of the orthorhombic.

The values of $\sin^2\theta$ for the rings in the Debye-Scherrer pattern due to *m*-xylene crystals are given in column 1 of Table I, and with these values the difference diagram was drawn according to Lipson's method. It was found from the diagram that the determination of the values of A, B, C from the equation

$$\mathrm{Sin}^2\theta = \mathrm{Ah}^2 + \mathrm{Bk}^2 + \mathrm{Cl}^2 \qquad \ldots \quad (1)$$

$$(\mathrm{A} = \lambda^2/4a^2, \quad \mathrm{B} = \lambda^2/4b^2 \quad \mathrm{C} = \lambda^2/4c^2).$$

was quite easy and all the rings could be indexed quite satisfactorily. The values of A, B, C determined in this way are A = .0098, B = .0083 and C = .0054. The axial lengths calculated from these values of A, B, C are : $a = 7.77$, $b = 8.45$, $c = 10.47$ Å. The values of $\sin^2\theta$ calculated with these axial lengths, the intensities of the Debye—Scherrer rings, the spacings and the indices are given in TableI, and it can be seen that the discrepancies between the calculated and observed values lie within the experimental error.

With these values of the dimensions of the unit cell and the value of the density determined in this investigation the number of molecules per unit cell was calculated and found to be 4.

The conditions limiting possible reflections indicated by Table I are

hkl *hko* *hol* *oko*	No condition	*hoo* : $h = 2n$ *ool* : $l = 2n$

Indian Journal of Physics, Vol. XXXIV, No. 6

PLATE IV

Fig. 1.

Fig. 2 *(a)*.

Fig. 2 *(b)*.

Fig. 3.

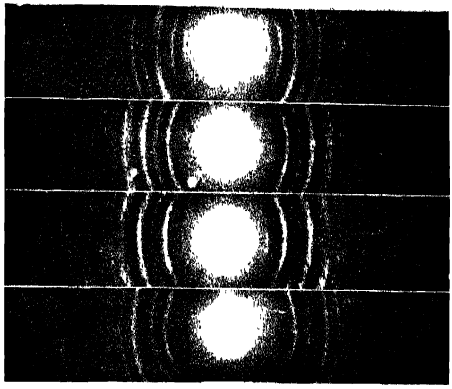

Fig. 1, Debye-Scherrer pattern of frozen *m*-xylene at −180°C
Fig. 2 *(a)*. Fibre like pattern of frozen *o*-xylene at −180°C
Fig. 2 *(b)*. Debye-Scherrer pattern of frozen *o*-xylene at −180°C
Fig. 3 Debye-Scherrer pattern of frozen *p*-xylene at −180°C

TABLE I

m-Xylene at −180°C

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Spacings (Å) (observed)	Indice
.0083 (s)	.0083	8 45	010
.0137 (s)	.0137	6.58	011
.0184 (vw)	.0181	5 08	110
.0215 (m)	0216	5 24	002
.0230 (m)	.0235	5.02	111
.0302 (m)	.0299	4.43	012
.0330 (w)	.0332	4.24	020
.0392 (s)	.0392 .0397	3.89	200 112
.0478 (m)	.0475 0484		210 121
.0530 (w)	.0529	3.34	211
.0547 (w)	.0548	3.25	022
.0606 (m)	.0608	3 13	202
.0648 (vw)	.0646	3 02	122
.0750 (vw)	.0747	2 81	030
.0801 (m)	.0801	2.72	031
.0865 (m)	.0864	2.62	004
.0938 (vw)	.0936 .0940	2.52	301 222
.1020 (vw)	1019	2.41	311
.1170 (w)	.1173	2.25	231
.1290 (w)	.1294	2.14	124
.1332 (m)	.1328 .1339	2.11	040 214
.1430 (w)	.1430 .1433	2.04	322 015
.1484 (w)	.1480	2.00	141
.1427 (w)	.1430	1.97	115
.1572 (vw)	.1568	1.94	400
.1746 (m)	.1746	1.84	304

Since the crystal belongs to the orthorhombic system and the unit cell contains molecules, the crystal belongs to the space group $P2_12_12$ or D_2^3

It can be seen from the above discussions that the number of molecules in the unit cell is the same as that required in the case of asymmetric molecules. The molecule may have either a plane of reflection perpendicular to its plane or a two-fold axis in its own plane. The plane cannot be utilised in the space group mentioned above and it is evident that the two-fold axis, if it is actually possessed by the molecule, does not coincide with any of the crystallographic axes.

(b) *Ortho-xylene at* 180°C

One of the many Debye-Scherrer patterns photographed for frozen *o*-xylene was found to be analogous to a pattern due to a fibre while the other photographs showed continuous rings. Figs. 2(a) and 2(b) plate III show these two types of photographs. The former type helped the correct assignment of the indices.

Lipson's method applied in this case also indicated the lattice to be orthorhombic. It was found, however, that while two of the axial lengths were identical with those for the *m*-xylene lattice, the primitive translation along the third axis had to be taken as almost double that for the meta compound in order to index all the reflections in the powder pattern.

The values of $\sin^2\theta$ observed in the pattern and those calculated from the values of A, B, C determined from the difference diagram, the spacings and the indices are given in Table II. It can be easily seen from Table II that the agreement between the observed and the calculated values of $\sin^2\theta$ is very satisfactory. The correctness of the indices has been verified by examining the positions of the maxima in the rings due to the fibrous specimen [Fig. 2(b)]. The values of A, B, C in this case are A = .0028, B = .0077, C = .0057, from which the dimensions of the unit cell have been calculated and found to be a = 14.55, b = 10.20 and c = 8.77 Å.

From the value of the density mentioned earlier and the axial lengths given above the number of molecules per unit cell was calculated and found to be 8. The values of $\sin^2\theta$ and the indices of the corresponding planes given in Table II show that there is no restriction limiting any reflection. So, the space group assigned to the crystal is Pmmm or D_2^1.

The molecule of *o*-xylene may have a plane of reflection perpendicular to the plane of the molecule and a two-fold axis in the plane of the molecule if the two CH_3 groups in the molecule form mirror images of each other in a vertical plane between them owing to their mutual orientation produced by steric repulsion. If the plane were parallel to any of the crystallographic plane the number of molecules per unit cell would be reduced to 4, but actually the number is 8.

Hence the plane of the molecule is inclined to the crystallographic axis forming a complicated structure.

TABLE II

o-Xylene at 180° C

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Spacings (Å) (observed)	Indices
0076 (ms)	0077	8 83	100
0086 (ms)	0085	8 30	011
0112 (vw)	0111	7 28	002
.0162 (vw)	.0162	6 09	111
0170 (vs)	0168	5 90	012
0228 (s)	.0228	5.10	020
0248 (s)	0245 .0250	4 89	112 003
.0310 (vs)	.0308	4 37	200
.0338 (vs)	0336 0339	4 19	201 022
.0442 (s)	0445	3.66	004
.0478 (s)	0476	3 52	212
.0507 (m)	0502 .0512	3 42	014 300
.0574 (m)	0579	3 21	114
.0644 (w)	.0646	3 03	222
0724 (vw)	.0721	2.86	301
.0812 (s)	0810	2 70	214
0866 (w)	0862	2 62	312
.0916 (vw)	.0914	2 54	040
.1034 (ms)	.1033 1035	2 40	322 134
.1174 (ms)	1171	2 25	323
1314 (ms)	1310	2.12	206
.1438 (vs)	.1434	2.03	144
.1595 (vs)	1591	1.93	136
.1778 (vs)	1780 .1773	1 83	008 431
.1835 (w)	.1837	1 80	018
.2012 (w)	2008 2010	1.72	028 511
.2048 (w)	.2050	1.70	344
.2408 (vw)	.2403	1.57	523

(c) *paraxylene at* $-180°C$:

The Debye-Scherrer pattern is reproduced in Fig. 3, Plate I. In determining the dimensions of the unit cell of the para compound it was noticed that the difference diagram did not yield sufficient number of constant differences. Hence Ito's method (Ito, 1950) was applied to index the pattern

In order to select the axial lengths a^*, b^*, c^* of the reciprocal unit cell it was observed that all the spacings of the planes *hoo*, *oko*, *ool* with h, k, l even observed in the case of the *m*-xylene crystal were also present in the Debye-Scherrer pattern due to the para compound. These reflections were first utilised in selecting the values of a^*, b^*, c^* The values are :

$$a^{*2} = 1/d^2_{100} = .0083, \quad b^{*2} = 1/d^2_{010} = .0138, \quad c^{*2} = 1/d^2_{001} = .0180$$

In order to select the reciprocal cell angles α^*, β^*, γ^*, (*hko*), (*hol*) and (*okl*) reflections were carefully examined and it was observed that some (*hko*) and (*okl*) reflections were present if the angles $a^* \wedge b^*$ and $b^* \wedge c^*$ were taken to be $90°$, and the angle $a^* \wedge c^*$ was calculated by studying some pairs of (*hol*) and (*hol*) reflections according to the equation

$$\cos\beta^* = \frac{1/d^2_{hol} - 1/d^2_{hol}}{4hla^*c^*} \qquad \ldots \quad (2)$$

where d_{hkl} is the spacing in the direct lattice

Thus the reciprocal cell-dimensions were calculated and found to be

$a^* = .0911$	$\alpha^* = 90°$
$b^* = .1174$	$\beta^* = 81°3'$
$c^* = .1339$	$\gamma^* = 90°$

With these values of the cell dimensions all the reflections in the powder pattern of the para xylene crystals were indexed according to the equation

$$1/d^2_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hla^*c^* \cos\beta^* \qquad \ldots \quad (3)$$

and the agreement was found to be satisfactory. The values of $1/d^2$ observed from the photograph and those calculated with the help of Eqn.(3), the intensities, and the indices are given in Table III The real cell corresponding to the reciprocal cell defines a lattice which is definitely the lattice of the crystal. The dimensions of the cell are

$$a = 7.56 \text{ Å}$$
$$b = 8.45 \text{ Å}$$
$$c = 11.11 \text{ Å}$$
$$\beta = 98°57'$$

TABLE III

p-Xylene at −180°C

$1/d^2$ (observed)	$1/d^2$ (calculated)	Indices
.0224 (vw)	0225	101
	0221	110
0301 (s)	0301	101
.0332 (m)	0332	200
.0366 (w)	0363	111
0437 (m)	0436	201
	0439	111
.0470 (s)	0470	210
.0550 (vs)	0552	020
.0720 (vs)	0722	002
0730 (w)	0732	021
	0729	102
0813 (w)	0813	301
.0886 (vs)	0884	220
	0885	310
	0881	102
0900 (vs)	0902	202
0994 (w)	0998	221
1032 (w)	.1031	301
1138 (s)	1140	221
1204 (w)	1206	202
.1242 (s)	.1241	302
1324 (m)	.1328	400
2066 (s)	2065	501
	2060	$30\bar{3}$
2208 (w)	2208	040
	.2212	421
	2213	510
	2207	023
	2215	203
2432 (vw)	2433	141
2595 (vw)	.2593	511
2750 (vw)	2744	303
.2925 (s)	2930	042
.3116 (vw)	3110	$24\bar{2}$
	3126	610
3445 (vw)	3440	024
3608 (w)	.3608	404
3830 (w)	.3834	143

Now it has to be found out whether this cell can be reduced further

Let the primitive cell in the direct lattice have edges a, b, c written in order of increasing dimensions, corresponding to reciprocal lattice obtained from Ito's method. Every translation $\boldsymbol{t}$ in the real lattice can be written in the form

$$\boldsymbol{t} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

where u, v, w are integers, positive or negative. The problem of finding out the reduced cell is simply that of finding three shortest non-coplanar t's with the values of a, b, c determined from a^*, b^*, c^* and β^*. These three t's then become the edges of the reduced cell. This can be easily done by computation after assigning different values to u, v, w, both positive and negative, and it has been found that the arbitrary cell itself, initially chosen for indexing the pattern, is the reduced cell. Again, since the edges of a reduced face of a unit cell in the direct lattice are the shortest translations of the net, they are shorter than either of the two diagonals of the cell. For this reason the projection of either of the cell edges on the other cannot be greater than half the other edge (Buerger, 1957). As a consequence of this it follows that in a reduced plane cell,

$$|a \cos \gamma| \leqslant \frac{b}{2} \quad \text{and} \quad |b \cos \gamma| \leqslant \frac{a}{2}$$

$$|ab \cos \gamma| \leqslant \frac{b^2}{2} \quad \text{and} \quad |ab \cos \gamma| \leqslant \frac{a^2}{2}$$

These relations also apply to the reduced three-dimensional cell.

The six scalar products $\boldsymbol{a}.\boldsymbol{a}, \boldsymbol{b}.\boldsymbol{b}, \boldsymbol{c}.\boldsymbol{c}, \boldsymbol{b}.\boldsymbol{c}, \boldsymbol{c}.\boldsymbol{a}, \boldsymbol{a}.\boldsymbol{b}$ have been taken as an exact representation of the cell, since the six parameters $a, b, c, \alpha, \beta, \gamma$ can readily be derived from them. For the purpose of identification, these six scalar products are set down in a form of rectangular matrix to represent the reduced cell as follows

$$\begin{pmatrix} \boldsymbol{a}.\boldsymbol{a} & \boldsymbol{b}.\boldsymbol{b} & \boldsymbol{c}.\boldsymbol{c} \\ \boldsymbol{b}.\boldsymbol{c} & \boldsymbol{c}.\boldsymbol{a} & \boldsymbol{a}.\boldsymbol{b} \end{pmatrix} = \begin{pmatrix} s_{11} & s_{22} & s_{33} \\ s_{23} & s_{31} & s_{12} \end{pmatrix}$$

Matrix representation of the direct cell of *p*-xylene crystal is found to be

$$\begin{pmatrix} 57.15 & 71.42 & 123\,40 \\ 0.00 & -12.92 & 0.00 \end{pmatrix} \qquad \ldots (7)$$

From representation (7) it can be seen that $\boldsymbol{a}.\boldsymbol{c}$ is less than either $\frac{1}{2}\boldsymbol{a}.\boldsymbol{b}$ or or $\frac{1}{2}\boldsymbol{b}.\boldsymbol{b}$. Hence according to (5) no further reduction is possible. From (7) it can also be seen that $s_{11} \neq s_{22} \neq s_{33}$, and since zero is regarded as negative (90° is regarded as obtuse angle for the purpose of identification) the standard cell is a primitive monoclinic one as indicated by Azaroff and Buerger (1958). With

the values of the dimensions of the unit cell given earlier and the density of the substance at $-180°C$ determined experimentally the number of molecules per unit cell has been calculated and found to be 4

The conditions limiting possible reflections for *p*-xylene crystals are

hkl	No condition
hol	No condition
oko	$k = 2n$

So the space group $P2_1/m$ has been assigned to the crystal

The *p*-xylene molecule may have a plane of symmetry perpendicular to the plane of the molecule and also a centre of symmetry with the two CH_3 groups oriented in a particular way. As regards the plane of reflection this particular space group cannot utilise the symmetry element as in that case the number of molecules would be reduced to two Again the contribution of the hydrogen atom in X-ray scattering is almost negligible Therefore, the centre of symmetry could have been utilised by the molecule to form the lattice and in that case the number of molecules per unit cell would be 2 Actually, however, the unit cell contains 4 molecules Hence it appears that the molecule does not possess the centre of symmetry in the solid state at $-180°C$.

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